Dynamic Control of Piezoelectricity Enhancement via Modulation of the Bulk Photovoltaic Effect in a BiFeO$_3$ Thin Film

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Piezoelectricity, which is an electromechanical effect induced by conversion between mechanical and electrical energy, is one of the key functionalities in ferroelectric oxides. Traditionally, structural engineering in synthesis via a variety of processing control parameters has been a well-established route to host so-called morphotropic phase boundaries for enhancing piezoelectricity. However, this involves dealing with synthetical complexity and difficulties of strictly controlling structures and defects. Instead, for simple and situ control, here, a critical pathway for light-induced piezoelectricity enhancement and its dynamic control is unveiled in a BiFeO$_3$/DyScO$_3$ thin film by implementing an in-plane geometry operation, allowing for modulation of the bulk photocatalytic effect. A series of in-plane length-dependent piezoresponse force microscopy and conductive atomic force microscopy-based measurements under illumination reveals its strong influence on the photocurrent and photovoltage, consequently revealing a maximum of eightfold increase of the effective piezoelectric coefficient, $d_{zz}$. Light polarization dependent measurements show sinusoidal behavior of piezoelectricity closely linked to photocurrent variations, leading to a further threefold increase of $d_{zz}$. Temporal decay measurements reveal persistent behavior of enhanced piezoelectricity after removal of illumination, associated with reemission of photocarriers trapped in sub-levels. These results pave the way for light-induced piezoelectricity enhancement compatible with the photovoltaic effect in ferroelectric thin films for multifunctional nano-optoelectronics.

1. Introduction

Structural engineering in synthesis via chemical doping and epitaxial strain has been established as a robust control parameter for a variety of functionalities in oxide thin films.[1–6] One such pronounced example is the strain-induced morphotropic phase boundary (MPB), serving as a key source for intriguing functionalities. In this regard, BiFeO$_3$ (BFO) has been considered a successful functional oxide with such MPB regions for largely enhanced electromechanica[7–9] and magnetoelectric coupling,[10,11] anisotropic conduction,[12,13] metal-insulator transitions,[14,15] photovoltaic effects,[16,17] and elastic softening.[18–20] Of all, the giant effective piezoelectricity coefficient, $d_{33}$, realized by phase boundary motion at the MPB, is particularly appealing for energy harvesting devices.[8] However, the prerequisite of synthesis to host MPB adds complexity, causing structural modification and thus resulting in rather an invasive way of enhancing piezoelectricity. Very recently, an alternative pathway of using light to induce a sevenfold enhancement of piezoelectricity was reported in a single crystal of BFO, offering simple and in situ control without altering its pristine structures.[21] The key factor is the bulk photovoltaic effect (BPV), resulting in generation of the open circuit voltage and photocarriers with their associated surface potential and doping density contributions respectively to piezoelectricity enhancement within the effective length of the bulk material. The BPV is only realized in non-centrosymmetric materials under illumination with higher energy than the bandgap, providing an essential source of significant electronic polarization, simulating the similar role as the p-n junction and Schottky barrier in conventional photovoltaics.[22,23] In addition to the symmetry requirement, material dimensions are also of critical importance for realization of the BPV. In case of thin films, however, the effective material length is the film thickness, typically ranging from 10’s to 100’s of nm, which is a limiting factor for sufficient realization of the BPV, hence light-induced piezoelectricity. Therefore, further investigations are needed on thin films to overcome such a limit for light-induced piezoelectricity enhancement for potential device implementation at the nanoscale.

Here, we show a pathway for dynamic control of enhanced piezoelectricity under illumination in a BFO/DyScO$_3$ (DSO) thin film by implementation of an in-plane geometry. We performed piezoresponse force microscopy (PFM) and conductive atomic
force microscopy (C-AFM) based measurements under illumination, revealing a locally enhanced piezoelectric signal depending on the in-plane electrode distance, and domain wall (DW) orientation due to their influence on the photocurrent and open circuit voltage from the BPV effect. Moreover, we show dynamic control of piezoelectric signals with their sinusoidal behavior closely linked to the photocurrent variations under polarization-resolved illumination, further proving that modulation of the BPV effect is the key control parameter. Temporal decay measurements show persistent piezoelectric signals associated with the trapping of photoinduced charges. These results establish the framework for dynamic control of piezoelectricity enhancement in a thin film via modulation of the BPV effect, offering its potential for applications in nano-optoelectronic devices.

2. Results and Discussion

A series of epitaxial BFO thin films were prepared to explore light-induced piezoelectricity enhancement, using different combinations: BFO on insulating substrates, such as DSO and ThScO$_3$ (TSO); BFO with a bottom electrode SrRuO$_3$ (SRO) on TSO; and BFO on an oxygen deficient substrate, SrTiO$_3$-d (STO). Details of the film structures and conditions characterized by X-ray diffraction are provided in the Supporting Information (Figure S1, Supporting Information). For the films with the insulating substrate and no bottom electrode, top gold electrodes were deposited and grounded by a needle contact, enabling an in-plane geometry operation between the tip and the top electrode. Ferroelectric domain structures of a BFO/DSO film were imaged by out-of-plane (OOP) and in-plane (IP) PFM phase scans at room temperature in dark, as shown in Figure 1. As can be seen, the OOP phase image shows almost uniform contrast, pointing in one direction, while the IP phase image shows stripe domains with a width of ≈150 nm, revealing the typical 71$^\text{°}$ domain configurations.$^{[24]}$ The schematic shows the crystal orientation and the polarization directions alternating between [111]$_{\text{pc}}$ and [111]$_{\text{pc}}$ directions, resulting in in-plane net polarization, $\vec{P}_{\text{net}}$. To investigate light-induced enhancement, using the photoelectric AFM setup (see Figure S2, Supporting Information for the details), local OOP PFM amplitude signals are measured by increasing the photon flux, $\Phi$ up to $1.3 \times 10^{19}$ cm$^{-2}$ s$^{-1}$, as shown in Figure 1c. We note that all of the PFM amplitude signals under illumination are rescaled by dividing them by the pristine signal (no illumination), indicating multipliers for enhancement, and also analyzed with Pearson correlation coefficients and t-test function for statistical insights (see Statistical Analysis section and Supporting Information for details). As a result, Figure 1c shows a characteristic evolution of the amplitude signal, first sharply increasing from the pristine value (up to $\Phi = 2.5 \times 10^{18}$ cm$^{-2}$ s$^{-1}$), and then gradually increasing to result in a saturation-like state, eventually revealing almost a sixfold enhancement of the PFM amplitude signal ($\Phi = 1.3 \times 10^{19}$ cm$^{-2}$ s$^{-1}$). Given that the excitation ac voltage, $V_{\text{ac}}$ used to measure the PFM amplitude signal is 1 V, and thus the measured PFM amplitude signal is directly proportional to the surface displacement, the effective piezoelectric coefficient, $d_{zz}$ is also found to show almost a sixfold increase, as a result of light-induced piezoelectricity enhancement. (For details, see the section on analysis of $d_{zz}$ and Figure S3, Supporting Information). Importantly, the same measurements on BFO/TSO show the same enhancement behavior, but the other BFO thin films with a bottom electrode (BFO/SRO/TSO) or conducting interfaces (BFO/STO) did not show such light-induced piezoelectricity enhancement due to the insufficient effective length of the material, being the film thickness of ≈200 nm. This can be explained by the recent model proposed for the realization of light-induced piezoelectricity enhancement in bulk BFO,$^{[21]}$ revealing the critical role of effective material length. The surface displacement generating the PFM amplitude signals are,$^{[25,26]}

$$D = D_{\text{meas}} + D_{\text{electrostatic}}$$

(1)

Which can be detailed further to:

$$D = d_{zz} V_{\text{ac}} + C' \left(V_{\text{ac}} - V_{\text{ip}}\right) V_{\text{ac}}$$

(2)

where $d_{zz}$ is the effective OOP piezoelectric coefficient, $C' = \frac{\partial C}{\partial z}$ is the derivative of the tip capacitance in the z-direction, $k$ is the effective contact elastic stiffness, and $V_{\text{ip}}$ is the surface potential. Under illumination, the BPV effect generates a local potential related to the open circuit voltage, $V_{\text{oc}}$, which in this case dominates the $V_{\text{ip}}$. Under this assumption, the total displacement would be rearranged as:

$$D = \left(d_{zz} - \frac{C'}{k} V_{\text{ac}}\right) V_{\text{ac}}$$

(3)

According to Sturman and Fridkin,$^{[27]}$ the $V_{\text{ac}}$ is given by:

$$V_{\text{ac}} = -\frac{J}{\left(\sigma_9 + \sigma_{\text{ph}}\right)} l$$

(4)

where $J$ is the BPV current, $\sigma_9$ and $\sigma_{\text{ph}}$ are the dark- and photoconductivity respectively, and $l$ is the effective device length. Therefore, the implementation of in-plane geometry without a bottom electrode or conducting interface for the thin film can provide the critical length regime to produce sufficient open circuit voltages for light-induced piezoelectricity enhancement.

To verify this role of the in-plane length, we performed a series of electrode distance (by moving the AFM-tip away) dependent measurements of local OOP PFM amplitude signals. First, the evolution of the rescaled PFM amplitude signals under illumination in two locations with different electrode distances is shown in Figure 2a. Throughout these measurements with electrode distances, the focus of laser light is under the AFM tip. Note that the evolution of PFM amplitude signals is equivalent to the evolution of $d_{zz}$, provided that $V_{\text{ac}}$ is 1 V, as previously mentioned. The inset describes the electrode distance by moving the AFM-tip away from it. Clear differences in enhancement are seen such that the rescaled amplitude signal ($\approx d_{zz}$) of the location with the shortest electrode distance (57 µm) is found to show more than a fourfold increase, whereas that of location with the furthest electrode distance (488 µm) results in almost an eightfold enhancement. This indicates clear dependence of the enhancement on the in-plane...
Figure 1. Light-induced piezoelectricity by implementation of in-plane geometry in a BFO thin film. a) Schematic of the in-plane film geometry for BFO with the resultant net polarization, \( P_{\text{net}} \) along the IP projection of two polarization variants along the \([111]_{\text{pc}}\) and \([111]_{\text{pc}}\) directions. b) IP and OOP (inset) PFM phase images of the BFO sample. c) Evolution of the rescaled OOP PFM amplitude signals with increasing the photon flux.

Figure 2. Further enhancement of piezoelectricity via modulation of the BPV through electrode distances and DW orientations. a) Electrode distance dependent enhancement of the rescaled OOP PFM amplitude signals with increasing the photon flux. b) Enhancement of the rescaled OOP PFM amplitude signals by increasing the electrode distance under illumination with the constant photon flux of \( 2 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1} \). c) Representative C-AFM based spectroscopic \( I-V \) curves for electrode distance dependent \( V_{\text{oc}} \) along the \( J_{/}D_W \) direction. The inset shows the \( I-V \) curve for the furthest electrode distance of 225 \( \mu \text{m} \) under the \( J/\text{DW} \) condition. d) Electrode distance dependent \( V_{\text{oc}} \) measured in macroscopic in-plane geometry.
length which should be associated with photovoltages due to the BPV effect. For more detailed analysis, the rescaled local PFM amplitudes are also measured under smaller increasing distance scales with the constant photon flux of $2 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$, as shown in Figure 2b, clearly revealing the increasing trend of light-induced piezoelectricity enhancement along with the increased in-plane length. Further, we investigated DW orientation dependence of enhanced piezoelectricity under illumination along distant locations by increasing electrode distances along two directions, defined by their associated photocurrent (J) directions parallel (J//DW) and normal (J⊥DW) to the DWs. As a result, the rescaled PFM amplitude signals qualitatively show larger light-induced enhancement at the furthest distance location (225 µm) along the J⊥DW direction than in the J//DW direction with a threefold and twofold increase from their value at the nearest (25 µm) location respectively. This implies the effect of DWs on the BPV effect, eventually affecting the light-induced piezoelectricity enhancement. For deeper insights into its link with the BPV effect, particularly on the role of the open circuit voltage ($V_{oc}$), C-AFM based spectroscopic I–V curves with the constant photon flux of $2 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$ are measured, as seen in Figure 2c. Clearly, the $V_{oc}$ along the J//DW direction is found to increase nearly proportionally with the electrode distance from $-4.7 \text{ V}$ (25 µm) to $-16.1 \text{ V}$ (70 µm) and eventually $-50 \text{ V}$ (225 µm). On the other hand, the $V_{oc}$ along the J⊥DW direction show a measurable value of $-8.2 \text{ V}$ only at the furthest electrode distance (225 µm), as shown in the inset. For more reliable and accurate investigations, macroscopic photovoltaic measurements were performed on a sample patterned by photolithography with precise electrode spacing from 10 to 200 µm. As shown in Figure 2d, the $V_{oc}$ is essentially found to be proportionally increasing with the increased electrode distance, further proving the role of effective in-plane material length on the generation of an internal electric field in the film.

In addition, the $V_{oc}$ is also found to be clearly dependent on the DW orientation, such that it is more largely increased in the case of J//DW than that of J⊥DW. This can be explained by the previous photoconductivity-driven study with the two resistance model,[24] pointing to higher effective resistance and thus lower conductivities for the case of J⊥DW, consequently resulting in a higher $V_{oc}$.

Given that piezoelectricity can be further enhanced via tuning of the BPV, we can also dynamically control it by varying light polarization using a half-wave plate (HWP), as schematically shown in Figure 3a. According to the following BPV effect equation, the photocurrent, $J_i$, along the $i$-th direction in the film:[27]

$$J_i = I_0 \beta_{ik} (e_i e_k^* + e_k e_i^*)$$

(5)

where $I_0$ is the light intensity, $\beta_{ik} = \beta_{ki}$ is a third-order tensor bearing the same symmetry as the piezoelectric tensor and describing the linear photocurrent, $e$ is the unit polarization vector of light, and $e^*$ is its conjugate vector. Due to the symmetric properties, the $\beta_{ik}$ tensor could be transferred into the form of a $3 \times 6$ tensor $\beta_i$. The tensor $\beta_i$ differs from zero only in the case of a non-centrosymmetric media. For a C$_{3v}$ point group symmetry, to which BFO belongs, the number of independent nonzero components of the $\beta_i$ tensor is four.[27] The photocurrents perpendicular and parallel to the in-plane projection of crystallographic directions along the [111]$_{oc}$ or [111]$_{op}$ axis of BFO are of interest here. Therefore, we define directions of the photocurrent, according to the in-plane projection of the crystallographic direction, which is the same as the direction of $P^{net}$. According to the phenomenological theory, the photocurrents of both monodomain and stripe domain thin films can be expressed in a simple form as the following:[24]

$$J_{\parallel} = A_{\parallel} \sin (4\theta) + Off_{\parallel}$$

(6)

$$J_{\perp} = A_{\perp} \cos (4\theta) + Off_{\perp}$$

(7)

where $J_{\parallel}$ and $J_{\perp}$ are the photocurrents collected perpendicular and parallel to the direction of $P^{net}$ respectively, $A_{\parallel}$ and $A_{\perp}$ are the photocurrent amplitudes of $\sin (4\theta)$ and $\cos (4\theta)$ dependencies for $J_{\parallel}$ and $J_{\perp}$ respectively, and Off$_{\parallel}$ and Off$_{\perp}$ are the photocurrent offsets independent of the light polarization.

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Figure 3. Dynamic control of piezoelectricity enhancement via light polarization. a) Schematic of light polarization dependent PFM (C-AFM) measurements by implementation of the half wave plate (HWP). b) The representative measurement on the electrode location of 225 µm along the J//DW direction of the rescaled PFM amplitude and photocurrent signals dependent on light polarization angles with a constant photon flux of $2 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$.

Note that the pristine PFM amplitude and photocurrent values are obtained before operating rotation of the light polarization angle.
Figure 4. Decay of piezoelectricity enhancement via photoconductivity. Temporal decay of the rescaled PFM amplitude signals dependent on electrode distances along the a) \( J/\parallel \)DW direction and b) the \( J\perp \)LDW direction. Inlet shows the representative decay of photocurrent signals for the electrode distance of 225 \( \mu \)m along the \( J\perp \)LDW direction. These measurement data are obtained by switching on and off the laser with the constant photon flux of \( 2 \times 10^{19} \) cm\(^{-2}\) s\(^{-1}\).

Consequently, the \( V_{oc} \) from Equation (4) is also associated with such photocurrent variations due to the light polarization, depending on \( J_{\perp} \) and \( J_{/\parallel} \):

\[
V_{oc} \text{ for } J_{\parallel} = -A_{1} \frac{\sin(4\theta_{1}) + Off_{1}}{\sigma_{2} + \sigma_{ph}} \tag{8}
\]

\[
V_{oc} \text{ for } J_{/\parallel} = -A_{1} \cos(4\theta_{1}) + Off_{1} \frac{1}{\sigma_{2} + \sigma_{ph}} \tag{9}
\]

As shown in Figure 3b, for the representative measurement on the electrode location of 225 \( \mu \)m along the \( J/\parallel \)DW direction, the rescaled OOP PFM amplitude signals show dynamics of their sinusoidal evolution induced by light polarization, spanning over a large range of values under illumination with the constant photon flux of \( 2 \times 10^{19} \) cm\(^{-2}\) s\(^{-1}\). This reveals the impact of polarization angle, leading to a further threefold enhancement of the PFM amplitude signal, in addition to the already enhanced signal induced by light. Moreover, dynamics of the rescaled photocurrent variations are shown, also revealing their sinusoidal behavior with the same trend as the PFM amplitude, indicating their correlation with a linear relationship. The same trend of the correlation between the PFM amplitude and photocurrent signals is seen for the case of electrode location of 225 \( \mu \)m along the \( J\perp \)LDW direction, as shown in Figure S4, Supporting Information.

Because the presence of the tunable BPV effect is the critical control parameter for the realization of light-induced piezoelectricity enhancement, further insights into its time-dependent behavior will provide a deeper understanding of optoelectronic properties. For this, we performed temporal decay measurements of enhanced OOP PFM amplitude (rescaled) signals along the \( J/\parallel \)DW and \( J\perp \)LDW (Figure 4a and 4b respectively) directions by switching on and off the laser for the constant photon flux of \( 2 \times 10^{19} \) cm\(^{-2}\) s\(^{-1}\). In the case of \( J/\parallel \)DW (Figure 4a), as expected from Figure 2b, the enhanced PFM amplitude signal by switching on the laser is rather small for the electrode distance of 25 and 75 \( \mu \)m with nearly zero generated \( V_{oc} \). Nevertheless, the \( V_{oc} \) is sufficiently large for the electrode distance of 225 \( \mu \)m. Interestingly, after removing illumination, the enhanced amplitude signal is not instantaneously decreased to its pristine value, showing exponential decay over a duration of 100 s. In addition, the resultant amplitude signal after switching off the laser for 100 s, is still higher than the pristine value, showing persistent behavior of the enhanced piezoelectricity. In the case of \( J\perp \)LDW (Figure 4b), the enhanced PFM amplitude signals are clearly seen with a proportionally increasing trend along with a larger electrode distance. After switching off the light, all these enhanced amplitude signals show exponentially decaying behavior over 200 s, reaching close to the pristine values before switching on the light. Importantly, we note that the photocurrent signals are rapidly reduced to zero within a few milliseconds, after switching off the light, as seen in the inlet of Figure 4b. However, the long-lived and exponential decay of PFM amplitude signals resembles the behavior of persistent photoconductivity as previously reported,[28] due to the role of trapped photocarriers. Based on this, we use the following model to explain the decay behavior of enhanced PFM amplitude signals along both \( J\perp \)LDW and \( J/\parallel \)DW directions, as supported by the two-step fitting in Figure S5, Supporting Information.

\[
\text{PFM}_\text{amp}(t) = \text{PFM}_\text{amp}(0) + A_{1}e^{-t/\tau_{1}} + A_{2}e^{-t/\tau_{2}} \tag{10}
\]

where PFM\(_{\text{amp}}(t)\) is the PFM amplitude signal at a specific time, PFM\(_{\text{amp}}(0)\) is the pristine PFM amplitude signal, \( t \) is the measuring time, \( A_{1} \) and \( A_{2} \) are the conductivity-related parameters, \( \tau_{1} \) and \( \tau_{2} \) are the decay time occurring over two steps (usually \( \tau_{1} \) refers to a direct recombination time, and \( \tau_{2} \) refers to the time of re-emitted carriers from trapping levels).[29] As a result of fitting this model (see Figure S5, Supporting Information for the details), we found for \( J\perp \)LDW that \( \tau_{1} \) and \( \tau_{2} \) are around 5.4 and 306 s respectively, and for \( J/\parallel \)DW that \( \tau_{1} \) and \( \tau_{2} \) are around 6.5 and 123 s respectively. These values are several orders of magnitude higher than the usual carrier lifetime on the order of several microseconds.[29] Under illumination, the photoinduced charge carriers initially reach an equilibrium state and fill the levels located under the Fermi level.[28,30] After switching...
off the light, apart from the direct recombination process, the trapped charge carriers are gradually re-emitted, leading to the prolonged decay time through a de-trapping process. This should be responsible for the persistent behavior of enhanced PFM amplitude signals. In the case of J⊥DW, as discussed by the two resistance models before, generation of higher \( V_{oc} \) than the case of J∥DW should further boost trapping of photoinduced charge carriers in sub-levels, thus allowing for longer survival of piezoelectricity enhancement.

3. Conclusions

In summary, we show a pathway for light-induced piezoelectricity enhancement by implementing an in-plane geometry of a BFO thin film, allowing for modulation of the BPV effect. Controlling the in-plane distance between the AFM tip and the electrode position, an eightfold enhancement of the pristine OOP PFM amplitude signal (\( \approx d_{\perp} \)) is achieved, revealing the key role of effective material length for sufficient realization of the BPV effect. We also show the dependence of piezoelectricity enhancement on the DW orientations, revealing higher enhancement in the case of J⊥DW than J∥DW, due to its larger \( V_{oc} \) values. Dynamic control of piezoelectricity with sinusoidal behavior is seen by control of light polarization, revealing another threefold enhancement, in addition to the already existing enhanced signal induced by light. Moreover, temporal decay measurements of enhanced piezoelectric signals under illumination show exponential decay, dependent on electrode distances and DW orientations, revealing the mechanism behind should be linked to trapping of photocarriers in sub-levels. These results establish a framework of light-induced piezoelectricity for BFO thin films, offering promising directions of ferroelectric thin films for multifunctional nano-optoelectronic devices.

4. Experimental Section

Sample Preparations: DyScO\(_3\) (DSO) and TbScO\(_3\) (TSO) single crystal substrates (SurfaceNet GmbH) were annealed in the oxygen-rich environment at 1050 °C for 2 h before loading in the pulsed laser deposition (PLD) chamber. Stripe domain BFO/DSO and BFO/TSO thin films with 71° DW patterns were grown on the bare (110)-oriented DSO and (110)-oriented TSO substrate respectively. BFO/DSO and BFO/TSO were deposited at 650 °C under an oxygen pressure of 0.15 mbar, and the pulse laser energy was set at 0.43 J cm\(^{-2}\) with a 10 Hz frequency. All the stripe domain thin films were ~300 nm thick. A 10–15 nm thick bottom electrode SrRuO\(_3\) (SRO) was used in BFO/SRO/TSO thin film fabrication. The SRO layer was deposited under an oxygen pressure of 0.20 mbar, and the pulse laser energy was set at 0.43 J cm\(^{-2}\) with a 5 Hz frequency. For BFO/STO, monodomains were grown on the STO (001)-oriented 4° miscut substrate with the deposition at 650 °C under an oxygen pressure of 0.15 mbar and the pulse laser energy was set at 0.43 J cm\(^{-2}\) with a 10 Hz frequency. For oxygen deficiency, the BFO/STO samples were annealed at high temperatures in an 80% N\(_2\) + 15% Ar\(_2\) + 5% H\(_2\) atmosphere. Further details of the BFO/STO growth and light polarization dependent measurements under illumination. Y.H., H.Z., and M.A. co-wrote the paper. Y.H., H.Z., and M.A. acknowledge China Scholarship Council and Warwick-China Scholarships.

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Y.H. and H.Z. contributed equally to this work. Y.H. and M.A. conceived the project. Y.H. and H.Z. designed the experiments. H.Z. fabricated the BFO thin films and performed macroscopic photovoltaic measurements between the top electrodes. Y.H. performed PFM, C-AFM, spectroscopy, and light polarization dependent measurements under illumination. Y.H., H.Z., and M.A. co-wrote the paper. Y.H., H.Z., and M.A. acknowledge

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The work was partly supported by the EPSRC (UK) through grant numbers EP/T027207/1 and EP/P025803/1. H.Z. acknowledges the China Scholarship Council and Warwick-China Scholarships.
D. Walker in the Department of Physics, University of Warwick for his supporting X-ray diffraction measurements during this work.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords**

BiFeO₃, bulk photovoltaic effect, ferroelectric, piezoelectricity, thin films

Received: July 13, 2022  
Revised: August 18, 2022  
Published online: